Removal of Uranium(VI) from Contaminated Sediments by Surfactants

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ABSTRACT

Uranium(VI) sorption onto a soil collected at the Melton Branch Watershed (Oak Ridge National Laboratory, TN) is strongly influenced by the pH of the soil solution and, to a lesser extent, by the presence of calcium, suggesting specific chemical interactions between U(VI) and the soil matrix. Batch experiments designed to evaluate factors controlling desorption indicate that two anionic surfactants, AOK and T77, at concentrations ranging from 60 to 200 mM, are most suitable for U(VI) removal from acidic soils such as the Oak Ridge sediment. These surfactants are very efficient solubilizing agents at low uranium concentrations: ca. 100% U(VI) removal for $[U(VI)]_{o,sorbed} = 10^{-6}$ mol kg^{-1}. At greater uranium concentrations (e.g., $[U(VI)]_{o,sorbed} = $ ca. 10^{-5} mol kg^{-1}), the desorption efficiency of the surfactant solutions increases with an increase in surfactant concentration and reaches a plateau of 75 to 80% of the U(VI) initially sorbed. The most probable mechanisms responsible for U(VI) desorption include cation exchange in the electric double layer surrounding the micelles and, to a lesser extent, dissolution of the soil matrix. Limitations associated with the surfactant treatment include loss of surfactants onto the soil (sorption) and greater affinity between U(VI) and the soil matrix at large soil to liquid ratios. Parallel experiments with H_2SO_4 and carbonate–bicarbonate (CB) solutions indicate that these more conventional methods suffer from strong matrix dissolution with the acid and reduced desorption efficiency with CB due to the buffering capacity of the acidic soil.

U RANIUM is a common contaminant at U.S. Department of Energy sites (a legacy of nuclear processing and weapon development) and at mine tailing sites associated with its production. Uranium is present as U(VI) and U(IV) in typical subsurface environments. In low pH solutions, U(VI) exists as the uranyl cation, UO_2^{2+}, while at higher pH, U(VI) hydrolyzes to form mono- and polynuclear complexes (e.g., $UO_2(OH)^+$, $UO_2(OH)_2$, $(UO_2)_3(OH)_5^+$, etc.). At pH greater than 6.5, carbonate complexes dominate other uranium species (Langmuir, 1978; Grenthe, 1992). These carbonate complexes are responsible for the mobility of uranium in oxidizing waters. Uranium sorption onto a wide variety of sorbents, including iron oxides, clays, and natural sediments, has been reported in the literature (e.g., Tripathi, 1983; Hsi and Langmuir, 1985; Payne and Waite, 1991; Waite et al., 1994). These studies reveal that pH and ionic strength can significantly influence the amount of uranium sorbed. Typical plots of the percentage of uranium sorbed on oxides and/or hydroxides versus pH exhibit the following features: (i) negligible adsorption at pH < 4, (ii) an adsorption edge at pH = 4 to 5, and (iii) a maximum adsorption at pH = 6 to 7. In the presence of CO_2, a desorption edge is observed at pH =

8 to 9. Depending on the conditions, similar pH effects can also be observed for U(VI) sorption on clays. The influence of ionic strength on adsorption of U(VI) is also reported in some of these studies: it is generally observed that the ionic strength has little effect on adsorption onto oxides and/or hydroxides. Conversely, it has been observed that, at low pH, ionic strength can have a significant influence on adsorption of U(VI) onto clays. The presence of both ionizable hydroxyl groups at edges of the clay particles and fixed negative charge sites resulting from isomorphic substitutions explains this result (Zachara and McKinley, 1993; McKinley et al., 1995; Turner et al., 1996). Cations such as sodium and calcium are able to compete effectively with UO_2^{2+} for these fixed negative charge sites (i.e., cation-exchangeable sites).

Given the significant health risks uranium poses, numerous polluted sites require decontamination. To avoid the high costs associated with excavation and disposal of contaminated soils in low-level radioactive waste sites, alternative technologies need to be developed. Furthermore, emphasis on in situ remediation schemes is warranted since those technologies are potentially more economical and reduce workers' exposure to contamination. Two recent Department of Energy reports describe the application of chemical treatments to the ex situ removal of uranium from Fernal, Ohio soils (Oak Ridge National Laboratory, 1993; Atomic Energy of Canada Limited, 1996). These treatments include CB, citrate, citrate–bicarbonate–dithionite (CBD), mineral acids (HCl, HNO_3, and H_2SO_4), chelators (EDTA, DTPA, and tiron), tiron–dithionite, and biphasic extraction. The CB and H_2SO_4 treatments appear to be most promising. The CB treatment is based on the formation of soluble complexes between U(VI) and CO_3^{2-} at pH of 8 to 9.5, while with H_2SO_4, the combination of matrix dissolution at pH < 2 and aqueous complexation with SO_4^{2-} effects uranium removal. Citrate or citric acid and the tiron–dithionite methods also show good results; however, as with the H_2SO_4 treatment, significant amounts of iron and aluminum are solubilized.

As an alternative to those chemical treatments, surface active agents (surfactants) might be used to remove toxic metals from contaminated soils. Surfactants are chemicals that, at low concentrations, adsorb onto surfaces and interfaces. At larger concentrations, surfactant molecules self-associate to form colloidal-size aggregates called micelles. The concentration at which micelles are first observed is called the critical micelle

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concentration (CMC). The amphiphatic character of the surfactant molecule, caused by the presence of both a hydrophobic group and a hydrophilic head group, is responsible for adsorption at interface and micellization. Depending on the nature of the hydrophilic group, surfactants are classified as nonionic (no apparent charge), cationic (positive charge), and anionic (negative charge). In ionic micelles, counterions are distributed into two regions: diffuse layer and Stern layer. Typical anionic surfactants contain one or more of the following head groups: sulfate, $-OSO_4^-$; sulfonate, $-SO_3^-$; or carboxylate, $-COO^-$. Studies have shown that, at concentrations greater than the CMC, surfactants with a specific head group could bind divalent cations. For instance cadmium, copper, zinc, and uranyl ions bind to micelles composed of anionic surfactants (Scamehorn et al., 1989; Tan et al., 1994; Reiller et al., 1994, 1996). This partitioning of cations in anionic micelles is usually modeled as an ion-exchange process (Quina and Chaimovich, 1979; Rathman and Scamehorn, 1984; Hafiane et al., 1991). Since the aforementioned studies were conducted in simple aqueous solutions without the presence of contaminated soil, the data cannot be directly used for evaluating the effectiveness of surfactants for removing strongly sorbing ions from soils.

In this paper, we test a surfactant treatment method for the removal of U(VI) from contaminated soils. After first characterizing U(VI) sorption onto a natural sediment obtained from the Oak Ridge National Laboratory (an iron oxide–coated clay–sand), the effects of several surfactants on desorbing uranium are compared with several chemical treatments including nitrilotriacetic acid (NTA), bicarbonate, and H_2SO_4. Controllable factors (e.g., surfactant structure and concentration, uranium concentration, equilibration time, and soil to liquid ratio) that may influence the efficiency of the desorption process are systematically evaluated in batch experiments.

MATERIALS AND METHODS

Chemicals

The following chemicals were used in this study: depleted uranyl oxynitrate (Alpha Easar, Ward Hill, MA), Witconate AOK and Witcolate ES2 (Witco Corporation, Greenwich, CT), Geropon T77 (Rhône-Poulenc, Cranbury, NJ), Dowfax 8390 (Dow Chemicals, Midland, MI), disodium salt of NTA and sulfuric acid (Aldrich, Milwaukee, WI), and sodium bicarbonate ($NaHCO_3$) and sodium sulfate (Na_2SO_4) (J.T. Baker, Phillipsburg, NJ). Stock solutions of uranium (2 and 0.02 mM) were prepared by mixing uranyl oxynitrate with deionized water (18.3 MΩ × cm). A dilute salt solution was prepared with $CaSO_4 \cdot 2H_2O$ (34 mg L^{-1}), $CaCl_2 \cdot 2H_2O$ (80.4 mg L^{-1}), $MgSO_4 \cdot 7H_2O$ (30 mg L^{-1}), NaCl (11.7 mg L^{-1}), and KCl (16.8 mg L^{-1}). The conductivity was 246 μS cm^{-1} and the pH = 5.6. All salts, acids (HCl, H_2SO_4, and HNO_3), and bases (NaOH and $NaHCO_3$) were American Chemical Society reagent-grade chemicals.

Soil Characterization

The soil was collected at a depth of 1 to 1.5 m at the midslope of the Melton Branch Watershed on the Oak Ridge Reservation, Oak Ridge, TN. The watershed has a shallow soil profile (0.5 to 2.5 m) underlain by fractured saprolite (Jardine et al., 1993). The soil was air-dried for several days and gently disaggregated, and the <2-mm fraction was collected. The pH of 1 g of soil in 10 mL of deionized water is 4. The soil texture is 25% clay, 35% silt, and 40% sand, determined by the hydrometer method (Gee and Bauder, 1986). The clay fraction is composed of illite (40%), mixed-layer illite and smectite (40%), kaolinite (20%), and traces of quartz (analyzed using X-ray diffraction by the New Mexico Bureau of Mines and Mineral Resources, Socorro, NM). Carbonates have been completely weathered and a large quantity of amorphous Fe and Mn oxides is present as coating (Jardine et al., 1993). Iron oxides were extracted using the CBD procedure and analyzed using inductively coupled plasma atomic emission spectroscopy (ICP–AES) (Jackson et al., 1986). The iron content, 32 g kg^{-1}, agrees with previously reported data for this soil (Arnseth and Turner, 1988; Kooner et al., 1995). The manganese content of a soil sample obtained from the same location was reported to range from 1 to 3 g kg^{-1} (Arnseth and Turner, 1988). Cation exchange capacity and fraction of organic carbon are 39 cmol kg^{-1} and 0.2%, respectively (analyzed by Energy Laboratories, Billings, MT). Soluble and exchangeable calcium concentrations are 0.06 mM and 14 × 10^{-3} mol kg^{-1}, respectively (Energy Laboratories). Concentrations of other soluble cations in the saturated soil range from 0.18 mM for Na$^+$ to 0.05 mM for Mg^{2+}. Additionally, the surface area of a soil sample obtained from the same location was reported to be ca. 40 m^2 g^{-1} (Kooner et al., 1995).

Experimental Procedure

The experiments consisted of two steps: (i) sorption of U(VI) onto the Oak Ridge soil and (ii) desorption from the soil. Here, sorption is operationally equated with measured removal of U(VI) from the aqueous phase and may include influences from precipitation. Likewise, desorption may include influences from dissolution. In the sorption experiments, a known amount of sediment (typically 1.00 g) was combined with a background electrolyte (1 mM NaCl and 1 mM $CaCl_2$ in deionized water) in 50-mL polypropylene centrifuge tubes. Uranium was added to the mixture from either a 2 or 0.02 mM uranyl nitrate stock solution. The final volume of the aqueous phase was 10 mL. The samples were then placed on an orbital shaker for 48 h. After centrifugation (10 000 rpm for 15 min), ca. 9.5 mL of supernatant was removed from each tube and its pH measured. Filtration of the solution was not deemed necessary as the supernatant appeared to be colloid-free. A subsample was diluted with deionized water and acidified with HNO_3 for determination of residual U(VI) in the aqueous phase. Sorption of U(VI) was studied as a function of time (equilibration period ranging from 1 to 168 h) and concentration of uranium (10^{-7} to 10^{-4} M). To study the influence of pH, U(VI) was added to the centrifuge tubes after a 72-h equilibration period to allow the system to reach equilibrium. During this period, pH was adjusted as necessary with HNO_3 and $NaHCO_3$. In some experiments, the calcium concentration was varied from 0 to 100 mM.

In the desorption step, a selected treatment solution (10 mL) was added to the previously contaminated soil. The centrifuge tubes were placed on the rotary shaker. Following the desorption period, the samples were centrifuged and 0.5 to 5 mL of the supernatant was collected, diluted with deionized water, and acidified for determination of the amount of U(VI) removed from the soil. The pH of the supernatant was also recorded. It should be noted that, unlike the sorption experiments, the pH of the soil solution was not adjusted during

the desorption step. The treatments included Na_2SO_4, NTA, bicarbonate, H_2SO_4, and surfactants. Desorption experiments with deionized water and salt solution were used as controls. Desorption times varied from 5 to 120 h. Treatment concentrations ranged from 25 to 200 mM. The concentration of sorbed U(VI) varied from ca. 10^{-6} to 10^{-3} mol kg^{-1} (i.e., initial U(VI) concentrations of 10^{-7} to 10^{-4} M and 1 g of soil 10 mL^{-1} of solution). Uranium(VI) desorption was also investigated for soil to liquid ratios of 0.1, 0.2, and 0.5 g mL^{-1}. In these experiments, the concentration of U(VI) initially added was 10^{-6} M; thus $[U(VI)]_{sorbed}$ = ca. 10^{-5}, 5×10^{-6}, and 2×10^{-6} mol kg^{-1} for 1, 2, and 5 g of soil 10 mL^{-1} of solution, respectively.

All samples were prepared in duplicate and some experiments were repeated several times. Controls containing only uranium or uranium and chemical treatments were also prepared to monitor uranium losses onto the container walls and to determine interferences from the added treatment on uranium determination via inductively coupled plasma mass spectrometry (ICP–MS). Uranium(VI) recovery ranged from 96 to 106%.

Sample Analysis

Uranium analysis was performed with ICP–MS (Perkin–Elmer, Norwalk, CT) with Bi (25 µg L^{-1}) as an internal standard. The U(VI) detection limit of this instrument is 10^{-10} M. The amount of U(VI) sorbed onto the sediment was determined based on the difference between the added and measured U(VI) concentration in the decanted solution. The amount of uranium desorbed by the chemical treatments was calculated using the ICP–MS data and was corrected for the small amount of liquid remaining following the sorption step. Iron was determined using a Perkin–Elmer ICP–AES.

RESULTS AND DISCUSSION

Uranium Sorption

In order to determine the equilibrium time for the U(VI) sorption studies, preliminary experiments were conducted to ascertain the sorption kinetics of uranium onto the Oak Ridge sediment. The rate of sorption is initially very fast (96.5% of the added uranium is sorbed in less than 1 h). This fast sorption step is followed by a slow reaction rate after a 48-h reaction period: U(VI) sorbed increases from 99.0 to 99.2% over 125 h (data not shown). Such a two-step kinetics is often reported for apparent adsorption of trace metals on clays and metal oxides and hydroxides (Hsi and Langmuir, 1985; Sparks, 1986; Waite et al., 1994). The fast sorption rate is attributed to uranium sorption onto readily available external surface sites, while the slow reaction rate corresponds to sorption onto less accessible sites and is controlled by diffusion of uranium into the sorbing phase. Based on these results, subsequent sorption experiments were conducted with a 48-h reaction time. It is important to note that the mechanism(s) responsible for removal of a solute from solution cannot be uniquely determined from macroscopic experiments such as those employed here. In particular, adsorption (accumulation of a solute at the soil–water interface; a two-dimensional process) and (co-)precipitation (formation of a new solid phase; a three-dimensional process) cannot be distinguished (Sposito, 1984, p. 234).

Sorption Isotherms

The amount of U(VI) sorbed versus U(VI) aqueous concentration is shown in Fig. 1a. Initial concentrations ranged from 10^{-7} to 10^{-4} M. The solid line represents a nonlinear fit of the data assuming a Freundlich-type sorption isotherm: $U(VI)_{sorbed} = K \times U(VI)_{aq}^{1/n}$. Models such as the Freundlich, linear, and Langmuir isotherms are often used to qualitatively describe sorption of trace contaminants (metals or organics) (Weber et al., 1991).
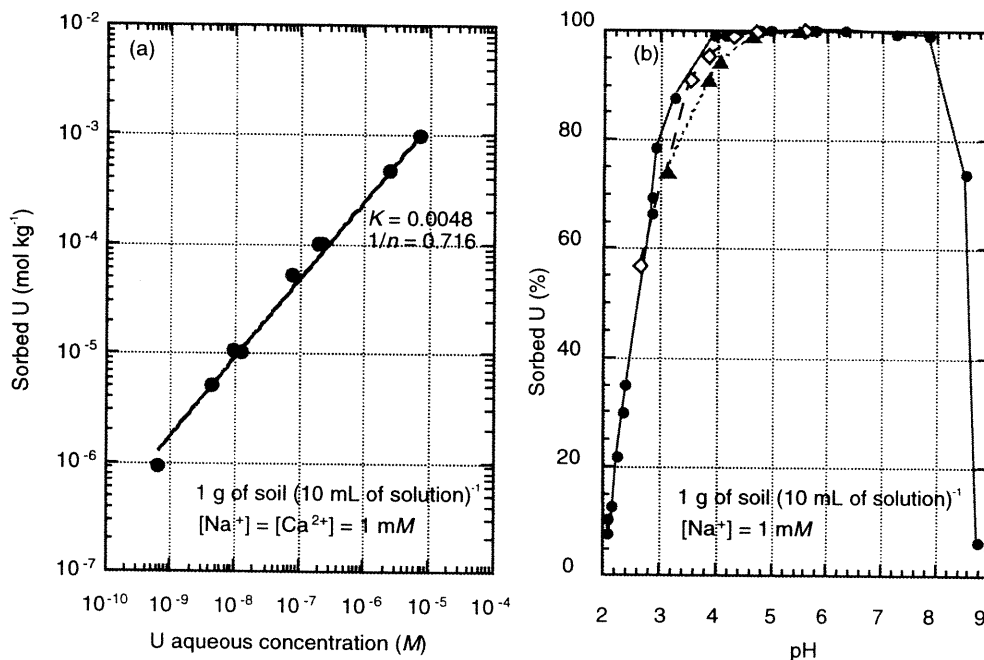

Fig. 1. (*a*) Uranium sorption isotherm. (●): $[U(VI)]_o$ = 10^{-7} to 10^{-4} M, $[Na^+]$ = $[Ca^{2+}]$ = 1 mM, and pH = 4 ± 0.05. K and $1/n$ are the Freundlich coefficients obtained using a nonlinear fit: $U(VI)_{sorbed}$ = $K \times U(VI)_{aq}^{1/n}$. (*b*) Uranium sorption as a function of pH. $[U(VI)]_o$ = 10^{-6} M. 1 g of soil 10 mL^{-1} of solution. [NaCl] = 1 mM and [CaCl$_2$] = 1 (●), 10 (◆), and 100 (▲) mM.

However, these empirical models, though widely used and useful in modeling contaminant transport, do not provide a full understanding of the sorption process, such as the influence of competing cations and pH. The U(VI) sorption isotherm shown in Fig. 1a significantly deviates from a linear sorption isotherm ($1/n = 0.716$), indicating that the distribution or partition coefficient, K_d ($K_d = [U(VI)]_{sorbed}/[U(VI)]_{aq}$), is a function of the uranium aqueous concentration. This result is often attributed to the heterogeneity of the adsorption sites. K_d ranged from 137 to 1448 mL g^{-1} for U(VI) aqueous concentrations of 7.2×10^{-6} to 6.4×10^{-10} M (pH = 4 ± 0.05 for all these samples).

Effect of pH and Competing Cation

The sorptive phases that control U(VI) sorption onto the Oak Ridge soil are probably the iron and manganese oxide coatings and the clay fraction. Specifically, hydroxyl groups on the oxide surface, –SOH, are expected to be the dominant sorption sites (Manceau et al., 1992). Hydroxylated groups (e.g., –SiOH and –AlOH) situated along the edges of clay minerals can also be significant sorption sites (Zachara and McKinley, 1993). Sorption onto such variable charge sites depends on the pH of the soil solution. As shown in Fig. 1b, U(VI) sorption onto the Oak Ridge soil is strongly influenced by the pH: one observes a sorption edge at pH = 2 to 4, followed by a maximum sorption at $4 < pH < 7.0$. A desorption edge is also present at pH > 8. Tripathi (1983), Hsi and Langmuir (1985), and Waite et al. (1994) have reported similar results for sorption of U(VI) onto synthetic sorbents such as goethite and ferrihydrite. It should be noted that these authors report adsorption edges at pH = 4 to 5; the lower sorption edge observed in our experiments could be caused by the heterogeneity of the soil: iron and manganese oxides, clays, and a small fraction of organic matter are all present. The pH dependence of the sorption process indicates that protons (H$^+$) compete with U(VI) for sorption sites (i.e., surface hydroxyl groups, –SOH): at low pH, H$^+$ is the principal sorbing species, forming positively charged diprotonated sites (–SOH$_2^+$). As the pH increases, U(VI) ions displace H$^+$ and bind to OH groups on the surface. The U(VI) reaction with those surface hydroxyl groups is similar to the hydrolysis reaction observed in aqueous solution only. Sorption of U(VI)–CO$_3^{2-}$ complexes is responsible for the large degree of U(VI) removal from the aqueous solution observed near neutral pH. The identity of these U(VI)–carbonate surface species is not yet resolved: Hsi and Langmuir (1985) have proposed sorption of UO$_2$(CO$_3$)SO$_2^{2-}$ and UO$_2$(CO$_3$)$_3^{4-}$ onto goethite; Payne and Waite (1991) have suggested UO$_2$CO$_3$, UO$_2$(CO$_3$)$_2^{2-}$, and UO$_2$(CO$_3$)$_3^{4-}$ sorption onto amorphous ferric oxyhydroxide (Fe$_2$O$_3 \cdot$ H$_2$O) (10); Waite et al. (1994) have proposed sorption of UO$_2$CO$_3$ onto ferrihydrite; and Duff and Amrhein (1996) have suggested that (UO$_2$)$_2$CO$_3$(OH)$_3^-$ is the sorbing species in the presence of goethite. Sorption of these U(VI) species has yet to be confirmed by direct spectroscopic evidences. Interestingly, the desorption edge observed at pH > 8 suggests that, in alkaline solutions, sorption of these U(VI)–carbonate complexes is limited.

Sorption of U(VI) onto fixed negative charge sites in clays at low pH has also been observed (Zachara and McKinley, 1993; McKinley et al., 1995; Turner et al., 1996). Monovalent and divalent cations such as Na$^+$ and Ca^{2+} could compete with the uranyl ions for these cation-exchange sites. To test this hypothesis, sorption experiments were conducted with varying Ca^{2+} concentrations (1, 10, and 100 mM) and controlled pH. Figure 1b shows that as the Ca^{2+} concentration increases, the adsorption edge shifts toward slightly higher pH, indicating that calcium has a minor but discernable influence on the amount of U(VI) sorbed. For example, at an equilibrium pH of 4.0, the amount of U(VI) sorbed is 99, 96, and 94% for Ca^{2+} concentrations of 1, 10, and 100 mM, respectively. It should be noted that it is not possible to unequivocally distinguish the cause of the observed effect (e.g., does Ca^{2+} compete with U(VI) for sorption sites?) since the addition of Ca^{2+} also increased the ionic strength of the soil solution (recall that these experiments were conducted with low level background electrolyte to approximate natural conditions).

The strong pH influence and the relatively minor effect of Ca^{2+} on sorption suggest that U(VI) is mostly sorbed onto amphoteric hydroxyl groups. The nature of the sorbed U(VI) species was not determined in this study. Previous X-ray spectroscopic studies of sorption onto iron oxides have shown that U(VI) forms bidentate inner-sphere complexes (Manceau et al., 1992; Waite et al., 1994). Thompson et al. (1998) have also reported the formation of U(VI) inner-sphere complexes with kaolinite. In light of these studies, one would expect U(VI) to form inner-sphere complexes on the Oak Ridge soil.

Uranium Desorption

A series of experiments were conducted to determine U(VI) desorption rate with a surfactant (T77) solution and a bicarbonate solution. The results show that, after a 5-h reaction time, the bicarbonate and surfactant released 37 and 7% of the sorbed U(VI), respectively. After 24 h, the desorption levels were 47% (bicarbonate) and 19% (surfactant). The amount of U(VI) released reached a plateau after 72 h (68 $\pm$ 2% for both treatment solutions). The reduced surfactant efficiency compared with the carbonate treatment during the initial stage of the desorption experiments may partly be caused by slower diffusion rates resulting from the much larger size of the surfactant micelles. Depending on surfactant structure and solution's conditions (i.e., ionic strength, temperature, etc.), surfactant micelles have sizes ranging from 50 to 200 Å. For comparison, the size of a carbonate molecule (CO$_3^{2-}$) is ca. 4 Å. Based on these results, subsequent desorption experiments were conducted over a 72-h equilibration time.

Choice of Surfactant and Chemical Treatment

Cationic surfactants were not selected since they would be lost through sorption onto the typically nega-

Table 1. Surfactant characteristics.

Surfactant	Head group	Description
AOK	$-SO_3^-$	Sodium C14–16 olefin sulfonate, 90% active, Mw = 324. Impurities are sodium salts (8%).
T77	$-CON(CH_3)CH_2CH_2SO_3^-$	Sodium oleyl n-methyl taurate, 72% active, Mw = 425. Impurities are sodium salts (25%).
ES2	$-(CH_2CH_2O)_2-OSO_3^-$	Sodium laureth sulfate (2EO), 26% active, Mw = 382. Impurities are water (50%) and sodium salts (24%).
D8390	$-C_6H_4(SO_3^-)-O-C_6H_4(SO_3^-)$	Mixture of disodium hexadecyldiphenyloxide disulfonate and disodium dihexadecyldiphenyloxide disulfonate, 40% active, Mw = 643. Impurities are water (58.5%) and sodium salts (1.5%).

tively charged soils. Selection among several anionic surfactants was based on their tendency to precipitate upon mixing with the background electrolyte (1 mM NaCl and 1 mM $CaCl_2$). This experiment eliminated surfactants such as sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate. Based on these preliminary results, the surfactants described in Table 1 were selected for the U(VI) desorption experiments. Other chemicals included for comparison were a chelating agent (NTA), sodium sulfate, sodium bicarbonate, and H_2SO_4. Desorption experiments with deionized water and the dilute salt solution were used as controls. Except for the acid and the carbonate, desorption experiments were conducted at 4.1 < pH < 5.4, where U sorption is near 100% (c.f., Fig. 1b). Also, it is important to note that UO_2^{2+} and UO_2^{2+} and $UO_2(OH)^+$ are the dominant U(VI) species in this pH range. Figure 2 presents U desorption and Fe solubilization for 1 g of soil initially contaminated with 10 mL of U(VI) at 10^{-6} M (i.e., amount of U(VI) sorbed equals ca. 10^{-5} mol kg^{-1}).

Water and the salt solution are very inefficient at releasing U(VI) from the sediment. Kinetics studies conducted with deionized water and the salt solution indicate that the amount of U(VI) desorbed from the Oak Ridge soil is less than 0.6% for equilibration times ranging from 24 to 120 h (data not shown). The lack of desorption observed with the salt solution supports the assumption that ion exchange is not responsible for U(VI) binding to the soil matrix. Approximately 14%

of the sorbed uranium was released using 60 mM of Na_2SO_4 (pH = 4.1). SO_4^{2-} forms aqueous complexes with UO_2^{2+} at pH of 2 to 7. However, the strength of these complexes does not permit significant desorption of U(VI) from the soil surface.

Nitrilotriacetic acid, a tetradentate ligand that has been suggested for in situ washing of metal contamination (Peters and Shem, 1992), can form complexes with UO_2^{2+} (log K = 11.5). However, <5% of the sorbed uranium was released from the soil upon mixing with NTA (60 mM) at pH = 5.4. Competition with other cations such as Fe^{3+} (log K = 18.2), Al^{3+} (log K = 13.8), and, to a lesser extent, Mn^{2+} (log K = 8.5) and Ca^{2+} (log K = 7.8), with which NTA forms stable complexes, might contribute to this result. For example, 123 mg L^{-1} of Fe was released with the NTA treatment. The relative inefficiency of NTA at desorbing U(VI) when compared with its effect on Fe solubilization could be caused by resorption of U(VI) onto the soil matrix. Alternatively, only a minor amount of U(VI) might have been associated with the Fe fraction solubilized by NTA. In contrast, 64.6 and 96.8% of the sorbed uranium was desorbed upon mixing with $NaHCO_3$ (60 mM, pH = 8.1) and H_2SO_4 (60 mM, pH = 1.9), respectively. The desorption mechanism of the $NaHCO_3$ treatment is the formation of aqueous uranium–carbonate complexes, which exhibit little affinity for the soil's sorption sites at pH > 8. Due to the buffering capacity of soils, such a high pH requirement reduces the efficiency of the bicarbonate
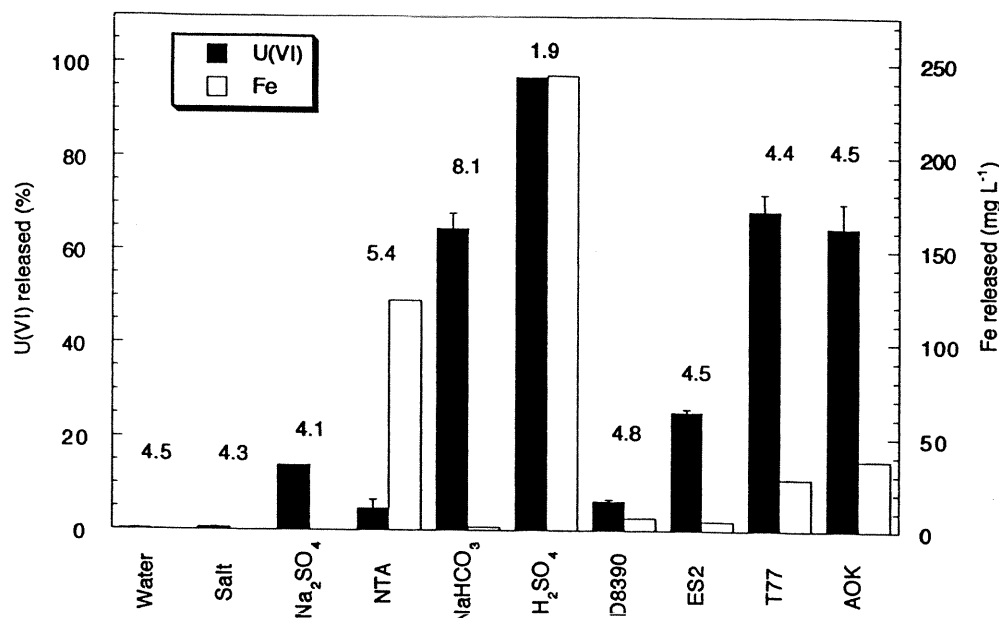

Fig. 2. Uranium and iron solubilization as a function of chemical treatments. $[U(VI)]_{o,sorbed}$ = ca. 10^{-5} mol kg^{-1}. Treatment concentrations are 60 mM. The pH of the soil solutions is indicated on the graph.

treatment for soils with acidic to neutral pH. Several mechanisms are responsible for the large degree of U(VI) desorption observed with H_2SO_4: (i) competition for active sites between H^+ and UO_2^{2+} is in favor of the hydrogen ion at this low pH (pH < 2), (ii) SO_4^{2-} forms aqueous U(VI) complexes, and (iii) H_2SO_4 dissolves parts of the soil matrix and therefore releases uranium associated with it. As an indication of this dissolution process, an Fe concentration of approximately 243 mg L^{-1} was measured following the H_2SO_4 treatment. This represents 7.5% of the iron content measured with the CBD extraction. The extremely acidic conditions and resulting mineral dissolution significantly limit the application of H_2SO_4 as a useful treatment agent. It should be noted that mineral dissolution has also been observed with less aggressive chemical treatments such as EDTA and citric acid (Oak Ridge National Laboratory, 1993). In contrast, the amount of Fe released by the bicarbonate treatment is negligible (<1 mg L^{-1}).

The effects of surfactants on U(VI) desorption from the soil is also presented in Fig. 2. T77 and AOK were the most efficient, with approximately 65% of U(VI) desorbed from the soil matrix. The pH of the soil solutions was ca. 4.45 for both surfactants. At this pH, the main uranium species are positively charged (85% SO_2^{2+} and 15% $UO_2(OH)^+$) and are then expected to be bound to the negatively charged micelles. Interestingly, the diphenyl oxide disulfonate surfactant, D8390, at pH = 4.75 released little uranium compared with AOK (6.3% versus 64.7%). While the active head group for AOK is a sulfonate group, $-SO_3^-$, the head group of D8390 contains two sulfonate groups linked to a phenyl ring: $-C_6H_4(SO_3^-)-O-C_6H_4(SO_3^-)$. Since D8390 possesses two negative charges, one might have assumed that D8390 would be more efficient at binding U(VI). However, the fraction of monovalent species is larger at higher pH (e.g., 25% $UO_2(OH)^+$ at pH = 4.75); thus, U(VI) binding to the D8390 surfactant could be expected to be less favorable. Less than 25% U(VI) removal was observed with ES2 at pH = 4.47. At pH = 2 and in aqueous solution only, SDS micelles were shown to bind >99% of U(VI) at concentrations ranging from 10^{-6} to 10^{-4} M (Reiller et al., 1994, 1996). At pH = 4.5, the amount of U(VI) bound to the micelles was reduced to 85%, presumably because of the lower UO_2^{2+} concentration. Since SDS and ES2 have related negatively charged head groups: $-OSO_3^-$ and $-(CH_2CH_2O)_2-OSO_3^-$, respectively, one would expect ES2 to bind U(VI) as efficiently. However, the amount of U(VI) released is likely to depend on several processes, including competition between sorption sites on the soil surface and binding sites at the water–micelle interface.

Desorption of U(VI) using anionic surfactants may be the result of ion-exchange reactions at the micelle surface, complexation with the surfactants, and soil matrix dissolution. The ion-exchange reaction takes place in the electric double layer (diffuse and Stern layers) surrounding the micelles. During ion exchange, U(VI) cations replace the Na^+ counterions. Previous studies suggest that monovalent cations such as $UO_2(OH)^+$ are "loosely" bound to the micelles, while divalent cations

(e.g., UO_2^{2+}) are strongly attached to the micellar surface and are specifically located in the Stern layer (Hafiane et al., 1991). In addition to the valence, size and hydration of the ions also influence binding at the micelle surface. Moreover, specific chemical interactions could be of importance at low concentrations (Hafiane et al., 1991). For instance, complexation reactions could occur between U(VI), a hard Lewis acid, and surfactant head groups containing donor atoms (i.e., S, O, or N). The length of the surfactant hydrophobic group, which affects micelle aggregation numbers and sizes, has also been shown to influence the fraction of U(VI) bound to anionic micelles (Reiller et al., 1994). The amount of U(VI) released from the soil matrix depends, to a certain extent, on the competition between sorption sites on the soil surface and binding sites at the micelle surface. The estimated number of surface sites in 1 g of the Oak Ridge soil ranges from ca. 2.5×10^{-6} mol measured by Kooner et al. (1995) to 1.5×10^{-4} mol, based on a site density of 2.31 sites nm^{-2} for bulk composite materials (Davis and Kent, 1990). The number of binding sites in 10 mL of surfactant solution is 6×10^{-4} mol based on a concentration of 60 mM and assuming that all the surfactant molecules participate in the exchange process. Given the degree of removal observed with T77 and AOK (ca. 65%), a comparison between the estimated number of sorption sites on the soil and the number of binding sites on the micelles suggest that these surfactants can compete efficiently with the soil matrix for U(VI). Surfactants can also dissolve a small fraction of the soil matrix. Evidence of this phenomenon is illustrated by the amount of Fe released during the desorption experiments: 28, 38, 5, and 7 mg L^{-1} for T77, AOK, ES2, and D8390, respectively. The largest levels of iron are obtained with T77 and AOK, the most efficient surfactants at releasing U(VI) from the soil. Interestingly, in parallel experiments, NTA released significant amounts of Fe while solubilizing less than 5% of the sorbed U(VI).

Based on the results presented above, T77 and AOK (and, for comparison, $NaHCO_3$) were chosen for subsequent studies designed to further evaluate the factors controlling desorption of U(VI) from contaminated soils.

Effect of Treatment Solution's Concentration and Sorbed Uranium(VI) Concentration

Uranium desorption as a function of the treatment solution's concentration is presented in Fig. 3a. Less than 40% of the sorbed uranium is desorbed at surfactant concentrations below 20 mM. The amount desorbed reaches a plateau at a surfactant concentration of 75 to 90 mM, after which the amount desorbed is ca. 75 to 80%. The pH of the soil solutions remained fairly constant during these experiments: pH = 4.6 ± 0.2. In the absence of soil, the CMC of these surfactants is ca. 1 mM. At sufficiently low concentrations, sorption could reduce the surfactant aqueous concentration below the CMC and prevent the formation of micelles. Additionally, sorbed surfactants may form aggregates, called ad-
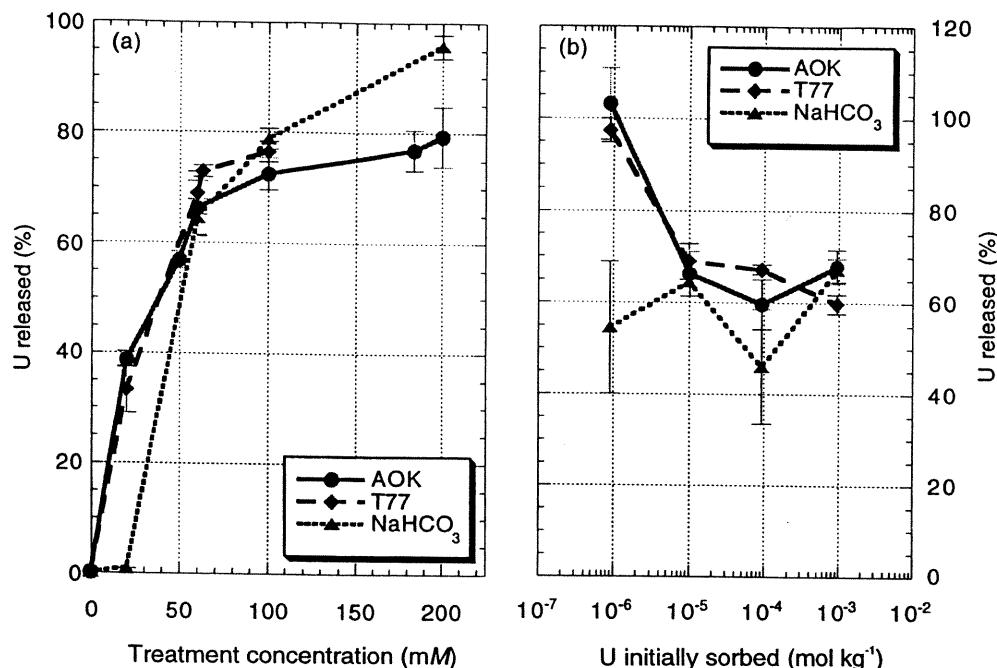
Fig. 3. (*a*) Uranium desorption as a function of the treatment concentration. $[U(VI)]_{o,sorbed}$ = ca. 10^{-5} mol kg^{-1}. (*b*) Uranium desorption as a function of the amount of uranium initially sorbed. $[U(VI)]_{added}$ = 10^{-7}, 10^{-6}, 10^{-5}, and 10^{-4} M. [Treatment] = 60 mM.

micelles, which could also bind solutes such as U(VI). However, surfactant sorption onto typically negatively charged soils is minimized by using anionic surfactants. Furthermore, as the overall surfactant concentration increases, loss of surfactants through sorption becomes less significant. Thus, as the surfactant concentration increases, the micelle concentration increases and greater release of U(VI) is observed. The amount of Fe solubilized increases as well: 10, 28, and 40 mg L^{-1} were measured in the T77 solutions at concentrations of 20, 60, and 100 mM, respectively. The plateau observed in Fig. 3a indicates that a substantial fraction of the U(VI) sorbed (ca. 20%) cannot be desorbed using the surfactant approach. The incomplete U(VI) release might be related to the fraction of U(VI) present in solution as UO_2^{2+} (20 ± 8% at pH = 4.6 ± 0.2). Additionally, surfactant–U(VI) complexes could be irreversibly sorbed onto the soil. In contrast, desorption of U(VI) with bicarbonate is negligible at a concentration of 20 mM (pH = 7.1). As the bicarbonate concentration increases, both pH of the soil solution and amounts of U(VI) released increase. Up to 90% of the uranium originally sorbed is released from the soil for a bicarbonate concentration of 200 mM. The equilibrium pH of the 60, 100, and 200 mM bicarbonate data points are 8.1, 8.2, and 8.5, respectively. The dramatic increase in desorption, from <1 to 64% for bicarbonate concentrations of 20 to 60 mM, respectively, correlates with the desorption edge shown in Fig. 1b: sorption is maximum at pH < 7.5 and then decreases drastically at pH > 8.

The effects of uranium concentration on the efficiency of the desorption treatments is illustrated in Fig. 3b. The pH of the soil solution remained constant for each treatment: 4.61 for AOK, 4.46 for T77, and 7.99 for

bicarbonate. The surfactants are highly efficient at low U(VI) surface coverages (ca. 10^{-6} mol kg^{-1}): approximately 100% of the sorbed uranium is released from the Oak Ridge soil. However, as the uranium loading increases, the amount of U(VI) desorbed appears to reach a plateau of ca. 60 to 70%. Conversely, the uranium concentration does not play a significant role when using the bicarbonate treatment: 62 ± 8% of U(VI) is desorbed regardless of the initial U(VI) surface coverage. The dissimilar responses of the treatments are further indication that the U(VI) release mechanisms for surfactants and bicarbonate differ. One would expect that U(VI) would primarily sorb onto high affinity sites and then, once those sites are saturated, sorption would shift to less reactive sites. Based on such assumptions, the efficiency of the desorption process would increase as the U(VI) surface concentration increases. Such a result, however, was not observed with the surfactants nor with the bicarbonate treatment. In light of these contradictory results, one might assume that other processes beside adsorption, such as precipitation, might be significant in the system studied here. Desorption levels might also be affected by U(VI) speciation in solution, a function of U(VI) concentration and treatment chemistry.

Effect of Soil to Liquid Ratio

The efficiency of all treatments was reduced as the soil to liquid ratio increased from 0.1 to 0.2 and then to 0.5 (Fig. 4). Decreased efficiency was most dramatic for the bicarbonate treatment: at a soil to liquid ratio of 0.2, the amount of U(VI) released form the soil was 17%, down from ca. 65% at a soil to liquid ratio of 0.1.
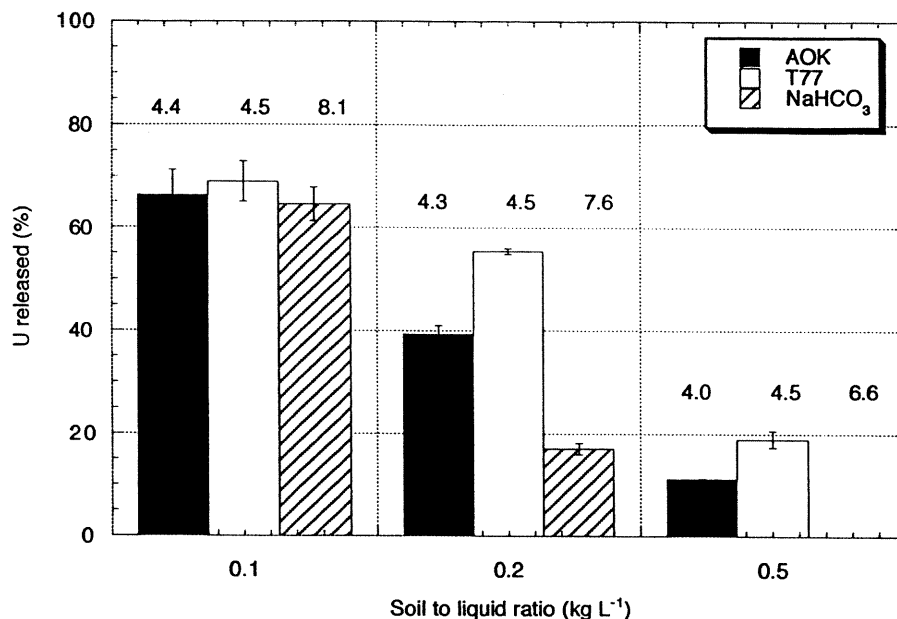
Fig. 4. Uranium desorption as a function of the soil to liquid ratio. [U(VI)]$_{o,sorbed}$ = ca. 10^{-5}, 5×10^{-6}, and 2×10^{-6} mol kg^{-1} for 1, 2, and 5 g of soil 10 mL^{-1} of solution, respectively. [Treatment] = 60 mM. The pH of the soil solutions is indicated on the graph.

No U(VI) was desorbed with a further increase in the soil loading (5 g in 10 mL). For similar ratios, the efficiency of the surfactant treatment decreased from 68 to 56 to 19% and from 65 to 39 to 12% for T77 and AOK, respectively. Several processes could explain the trend observed in Fig. 4. The number of U(VI) and surfactant sorption sites increases as the soil to liquid ratio increases. Surfactant sorption is enhanced and, therefore, the surfactant concentration in the aqueous phase is reduced. An indirect confirmation of surfactant loss is the lower amount of Fe solubilized as the amount of soil increases: Fe concentrations in the supernatant decreased from 28 to 13 mg L^{-1} and from 38 to 7.6 mg L^{-1} as the soil to liquid ratio increased from 0.1 to 0.5 for T77 and AOK, respectively. The drastic decrease in U(VI) solubilization with the bicarbonate treatment could be caused both by sorption of bicarbonate ions and the buffering capacity of the Oak Ridge soil. Sorption of bicarbonate decreases the aqueous concentration of U(VI) ligands, while the acidic soil reduces the pH of the soil solution. This combined effect could be responsible for the bicarbonate treatment's greater sensitivity to the soil to liquid ratio. In our experiments, the pH of the soil solution decreases from 8.1 to 7.6 and then to 6.6 for soil to liquid ratios of 0.1, 0.2, and 0.5, respectively (note that the pH of the surfactant-treated samples is relatively insensitive to the soil to liquid ratios). As shown in Fig. 1b, U(VI) maximum sorption occurs at pH = ca. 6.5. Additionally, as the amount of soil increases, the number of high affinity sorption sites and concentration of reactants forming low-solubility complexes and precipitates increases as well. Concurrently, the U(VI) sorbed concentration decreases from ca. 10^{-5} to 2×10^{-6} mol kg^{-1}. As a result, U(VI) is bound more tightly to the soil, and thus the efficiency of any solubilizing solution is reduced.

IMPLICATIONS FOR REMEDIATION OF CONTAMINATED SOILS

Release of U(VI), tightly bound through specific interactions (i.e., chemisorption and possibly precipitation), from an iron oxide–coated clay–sand soil, obtained from the Oak Ridge National Laboratory, is not trivial. Mild chemical treatment solutions such as salt solutions are ineffective. More aggressive treatment by H$_2$SO$_4$ can desorb U(VI) efficiently. However, the strong matrix dissolution by the acid prevents its application as a useful agent for in situ removal of U(VI). Bicarbonate can also desorb U(VI); however, the desorption efficiency is severely reduced by the buffering capacity of the acidic soil. As an alternative to these treatment solutions, two anionic surfactants, AOK and T77, were found most suitable for U(VI) removal from the contaminated soil. The most likely mechanisms responsible for U(VI) desorption include cation exchange in the electric double layer surrounding the micelles and, to a lesser extent, dissolution of the soil matrix. These surfactants are very efficient solubilizing agents at low uranium concentrations. The desorption efficiency of the surfactant solutions was also shown to increase with an increase in surfactant concentration. Limitations associated with the surfactant treatments were identified. Surfactant sorption onto the soil and greater affinity between U(VI) and the soil matrix reduce the efficiency of the treatment solutions at large soil to liquid ratios. This result indicates that remediation of the Oak Ridge soil with the selected surfactants (or the bicarbonate treatment) will not be effective using an in situ approach. Acidic soils with lower oxide and clay contents would be the preferred candidates for such an in situ surfactant treatment. Due to the cation exchange nature of the desorption process, the presence

of competitive cations could reduce the amount of U(VI) removed from the soil. However, the nonspecificity of the desorption process suggests that these surfactants could be used to remove other hazardous or radioactive cations (e.g., Cd^{2+}, Pb^{2+}, Co^{2+}, Sr^{2+}, etc.) from contaminated soils.

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